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Time-convolutionless master equation dynamics for charge-transfer processes between semiconducting polymers

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The dynamics of charge transfer between molecular species in the condensed phase remains a difficult and compelling problem from a theoretical perspective. The difficulty stems from the fact that one is faced with the situation that for most of the time there is a clear separation in the time-scales between the motion of the electronic degrees of freedom and the nuclear or molecular degrees of freedom. Hence, most of the time, nuclear reorganization dynamics following some dramatic change in the electronic structure occurs on the Born-Oppenheimer potential energy curves parameterized by the nuclear coordinates. However, this description breaks down whenever the electronic wave function changes rapidly in the direction of the nuclear motion leading to transitions between the discrete electronic states. This coupling becomes even more dramatic when there is an actual crossing of the potential curves at certain nuclear geometries. Even more so, the number of nuclear degrees of freedom, while finite, typically far out number the number of relevant electronic states for a given process.

For the case of a infinite thermostat, the Pauli master equation and Redfield equation have long been applied to the study of quantum relaxation. While originally derived from more or less heuristic arguments, such equations can be obtain from formally exact master equations using projection operator techniques and a series of well defined approximations. In the limit of a continuum of modes, the resulting transition probabilities become identical to what one obtains using Fermi's golden rule.

In this paper, we review our recent work in deriving a formally exact and time-local approach for incorporating non-Markovian dynamics in to the quantum master equation for state to state electronic transitions. [1] Here, we discuss some of the details of this work with particular attention to its theoretical development. As an application, we examine the kinetics of charge transfer between two co-facially stacked conjugated polymer chains [2, 3, 4] using a model recently developed by our group. [5] Here we compare the inclusion of both fast and slow phonon modes affect the transfer of a hole from one chain to the next following photo-excitation.

The Hamiltonian describing a wide range of photophysical problems can be cast in the form:

$$H = \sum_n \epsilon_n |n\rangle\langle n| + \sum_{nmi} g_{nmi} |n\rangle\langle m|(a_i^\dagger + a_i) + \sum_i \omega_i a_i^\dagger a_i. \quad (1)$$

Here $|n\rangle$'s denote electronic states with vertical energies ϵ_n , a_i^\dagger and a_i are the creation and annihilation operators for the normal mode i with frequency ω_i , and g_{nmi} are the coupling parameters of the electron-phonon interaction which we take to be linear in the phonon normal mode displacement coordinate.

We can separate H into a part that is diagonal with respect to the electronic degrees of freedom,

$$H_0 = \sum_n \epsilon_n |n\rangle\langle n| + \sum_{ni} g_{nni} |n\rangle\langle n|(a_i^\dagger + a_i) + \sum_i \omega_i a_i^\dagger a_i, \quad (2)$$

and an off-diagonal part V

$$V = \sum'_{nmi} g_{nmi} |n\rangle\langle m|(a_i^\dagger + a_i), \quad (3)$$

where the prime at the summation sign indicates that the terms with $n = m$ are excluded. This separation is useful for the following two reasons. First, in many systems only off-diagonal coefficients g_{nmi} are small compared to g_{nni} . Hence, V can be treated as a perturbation. Second, for many cases of interest, the initial density matrix commutes with H_0 . In this case, the separation gives simpler forms of the master equations.

For further analysis it is convenient to perform a polaron transform using

$$U = e^{-\sum_{ni} \frac{g_{nni}}{\omega_i} |n\rangle\langle n|(a_i^\dagger - a_i)} = \sum_n |n\rangle\langle n| e^{-\sum_i \frac{g_{nni}}{\omega_i} (a_i^\dagger - a_i)} \quad (4)$$

in which our transformed Hamiltonian becomes

$$\tilde{H}_0 = U^{-1} H_0 U = \sum_n \tilde{\epsilon}_n |n\rangle\langle n| + \sum_i \omega_i a_i^\dagger a_i, \quad (5)$$

where the renormalized electronic energies are

$$\tilde{\epsilon}_n = \epsilon_n - \sum_i \frac{g_{nni}^2}{\omega_i}. \quad (6)$$

Applying the same unitary transformation to V gives

$$\tilde{V} = \sum_{nmi} |n\rangle\langle m| M_{nmi}, \quad (7)$$

where the system-bath operators are

$$M_{nmi} = g_{nmi} \left(a_i^\dagger + a_i - \frac{2g_{nni}}{\omega_i} \right) e^{\sum_j \frac{(g_{nnj} - g_{mmj})}{\omega_j} (a_j^\dagger - a_j)}. \quad (8)$$

At this point it is useful to connect the various terms in our Hamiltonian with specific physical parameters. The terms involving $(g_{nnj} - g_{mmj})/\omega_j$ can be related to the reorganization energy

$$E_{nm}^\lambda = \sum_j \frac{(g_{nnj} - g_{mmj})^2}{\omega_j^2} = \sum_j \hbar\omega_j S_j$$

where S_j is the Huang-Rhys factor for mode j which is related to the Franck-Condon factor describing the overlap between the $v_j = 1$ vibronic state in one electronic state with the $v_j = 0$ vibronic state in the other. Likewise, the energy difference between the renormalized energies is related to the driving force of the transition,

$$\Delta E_{nm} = \tilde{\epsilon}_n - \tilde{\epsilon}_m.$$

In the transformed picture the electronic transitions from state $|n\rangle$ to $|m\rangle$ are accompanied not only by the creation or annihilation of a single phonon of mode i but also by the displacements of all the normal modes. This is quite different from the spin-boson model which does not have coordinate dependent coupling between the electronic states.

For a properly chosen projection operator \mathcal{P} and the initial total density matrix that satisfies $\rho(0) = \mathcal{P}\rho(0)$, $\mathcal{P}\rho(t)$ can be shown to satisfy at least two different master equations: the Nakajima-Zwanzig (NZ) equation [6, 7, 8] and the time-convolutionless (CL) master equation [9].

$$\frac{\partial \mathcal{P}\rho(t)}{\partial t} = - \int_0^t d\tau \mathcal{K}^{NZ}(t-\tau) \mathcal{P}\rho(\tau), \quad (9)$$

$$\frac{\partial \mathcal{P}\rho(t)}{\partial t} = - \int_0^t d\tau \mathcal{K}^{CL}(\tau) \mathcal{P}\rho(t). \quad (10)$$

The explicit expressions for superoperators $\mathcal{K}^{NZ}(\tau)$ and $\mathcal{K}^{CL}(\tau)$ can be found in Ref. [10]. Since Eq. 10 is less well known than Eq. 9 we will show here how Eq. 10 can be derived from Eq. 9. Applying the Laplace transformation to both sides of Eq. 9 we obtain

$$s\mathcal{P}\rho(s) - \mathcal{P}\rho(0) = -\mathcal{K}(s)\mathcal{P}\rho(s), \quad (11)$$

where $\rho(s)$ and $\mathcal{K}(s)$ are the Laplace transforms of $\rho(t)$ and $\mathcal{K}(t)$, respectively. Solving the last equation for $\rho(s)$ and applying the inverse Laplace transformation we have the formal solution of Eq. 9

$$\mathcal{P}\rho(t) = \mathcal{V}(t)\mathcal{P}\rho(0), \quad (12)$$

where

$$\mathcal{V}(t) = \frac{1}{2\pi i} \int_{\kappa-i\infty}^{\kappa+i\infty} \frac{e^{st}}{s + \mathcal{K}(s)} \quad (13)$$

and κ is an arbitrary positive constant chosen so that the contour of integration lies to the right of all singularities of the integrand. Differentiating Eq. 12 with respect to time we obtain the time local master equation

$$\frac{\partial \mathcal{P}\rho(t)}{\partial t} = \mathcal{F}(t)\mathcal{P}\rho(t) \quad (14)$$

with

$$\mathcal{F}(t) = \frac{\partial \mathcal{V}(t)}{\partial t} \mathcal{V}^{-1}(t). \quad (15)$$

Eq. 14 can be written in the form of Eq. 10 with

$$\mathcal{K}^{CL}(\tau) = -\frac{\partial \mathcal{F}(\tau)}{\partial \tau}. \quad (16)$$

Even though Eqs. 9 and 10 are formally exact, it is impossible to determine $\mathcal{K}^{NZ}(\tau)$ and $\mathcal{K}^{CL}(\tau)$ for most realistic systems. Since we have assumed the coupling to be weak, we ond order in the coupling constants

$$\mathcal{K}_2^{NZ}(\tau) = \mathcal{K}_2^{CL}(\tau) = \mathcal{P}\mathcal{L}_V e^{-i\mathcal{L}_0\tau} \mathcal{L}_V \mathcal{P}. \quad (17)$$

Here \mathcal{L}_0 and \mathcal{L}_V are the Liouville superoperators corresponding to \tilde{H}_0 and \tilde{V} whose action on some density matrix ρ is given by

$$\mathcal{L}_0\rho = \tilde{H}_0\rho - \rho\tilde{H}_0, \quad \mathcal{L}_V\rho = \tilde{V}\rho - \rho\tilde{V}. \quad (18)$$

In Ref. [10], Breuer and Petruccione show that to second order in the coupling constants, the convolutionless experession (Eq. 10) gives a better approximation to the exact solution than the Nakajima-Zwanzig equation (Eq. 9). It also has an additional mathematical convenience of being local in time. Therefore, in the following analysis we will use the convolutionless approach.

Taking our initial density matrix in the transformed representation as

$$\tilde{\rho}(0) = |n\rangle\langle n| \frac{e^{-\beta\sum_i \omega_i a_i^\dagger a_i}}{\text{Tr}(e^{-\beta\sum_i \omega_i a_i^\dagger a_i})}. \quad (19)$$

we will use the projection operator that acts on the total density matrix in the following way

$$\mathcal{P}\rho = \sum_n |n\rangle\langle n| \rho_{eq}^{os} \text{Tr}(|n\rangle\langle n|\rho), \quad (20)$$

where the trace is taken over both electronic and oscillator degrees of freedom and

$$\rho_{eq}^{os} = \frac{e^{-\beta \sum_i \omega_i a_i^\dagger a_i}}{\text{Tr}(e^{-\beta \sum_i \omega_i a_i^\dagger a_i})}. \quad (21)$$

Note that

$$\text{Tr}(|n\rangle\langle n|) = P_n, \quad (22)$$

where P_n is the probability to find the electronic subsystem in state $|n\rangle$. Using Eq. 10, the definition of $\mathcal{K}_2^{CL}(\tau)$ in Eq. 17, and the definition of $\mathcal{P}\rho$ given by Eq. 20 the following explicit convolutionless equation is obtained

$$\frac{dP_n}{dt} = \sum_m W_{nm}(t)P_m - \sum_m W_{mn}(t)P_n. \quad (23)$$

The time dependent rates $W_{nm}(t)$ are given by

$$W_{mn}(t) = 2\Re e \int_0^t d\tau \sum_{ij} \langle M_{nmi} M_{mnj}(\tau) \rangle e^{-i(\tilde{\epsilon}_n - \tilde{\epsilon}_m)\tau}, \quad (24)$$

where

$$\langle M_{nmi} M_{mnj}(\tau) \rangle = \text{Tr}(M_{nmi} M_{mnj}(\tau) \rho_{eq}^{os}). \quad (25)$$

Due to the explicit form of operators M_{nmi} (Eq. 8) the calculation of the correlation functions in Eq. 25 can be reduced to the averaging of the displacement operators over the equilibrium ensemble (Eq. 21). After straightforward, but lengthy, calculations we obtain the principal result of our work:

$$\begin{aligned} \langle M_{nmi} M_{mnj}(\tau) \rangle &= g_{nmi} g_{mnj} \\ &\times ((\Delta_{nmi}(\bar{n}_i + 1)e^{i\omega_i\tau} - \Delta_{nmi}\bar{n}_i e^{-i\omega_i\tau} + \Omega_{nmi}) \\ &\times (\Delta_{nmj}(\bar{n}_j + 1)e^{i\omega_j\tau} - \Delta_{nmj}\bar{n}_j e^{-i\omega_j\tau} + \Omega_{nmj}) \\ &+ \delta_{ij}(\bar{n}_i + 1)e^{i\omega_i\tau} + \delta_{ij}\bar{n}_i e^{-i\omega_i\tau}) q_{nm}(\tau) f_{nm}(\tau). \end{aligned} \quad (26)$$

Here

$$\Delta_{nmi} = \frac{(g_{nni} - g_{mmi})}{\omega_i}, \quad (27)$$

$$\Omega_{nmi} = \frac{(g_{nni} + g_{mmi})}{\omega_i}, \quad (28)$$

$$\bar{n}_i = \frac{1}{e^{\beta\omega_i} - 1}, \quad (29)$$

$$q_{nm}(\tau) = e^{i\sum_j \Delta_{nmj}^2 \sin \omega_j \tau}, \quad (30)$$

$$f_{nm}(\tau) = e^{-2\sum_j (\bar{n}_j + \frac{1}{2})\Delta_{nmj}^2(1 - \cos \omega_j \tau)}. \quad (31)$$

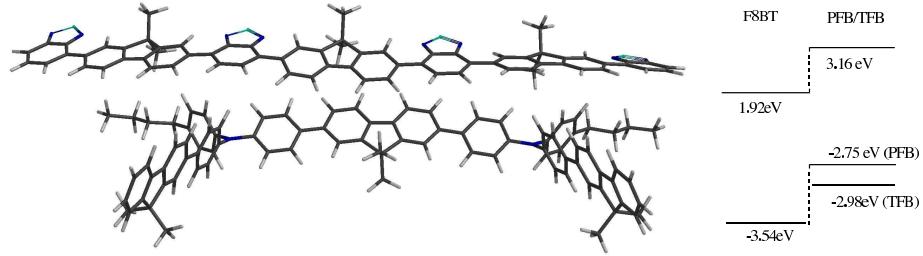
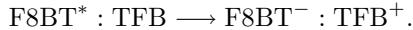


FIG. 1: (Left) Molecular geometry of TFB:F8BT interface. (Right) Relative energies of highest occupied and lowest unoccupied orbitals of TFB and F8BT.

In the case when all the diagonal electron/phonon terms vanish, $g_{nni} = 0$, the correlation functions in Eq. 26 reduce to those obtained within the golden rule approach [11, 12]. It is clear from Eq. 26 that for systems with $g_{nni}/\omega_i \gg 1$ the golden rule approach is not applicable. Unfortunately, the complicated form of the correlation functions precludes much further analysis at this point and we need to turn to numerical calculations.

As an application of our approach, we consider the electronic relaxation in the conjugated polymer heterojunctions previously investigated in Ref. [13, 14] by a different approach. Here we consider the decay of an excitonic state into a charge-separated state at the interface between two semiconducting polymer phases (TFB) and (F8BT). The structure of the polymers at the interface is shown in Fig. 1. Such materials have been extensively studied for their potential in organic light-emitting diodes and organic photovoltaics [4, 15, 16]. At the phase boundary, the material forms a type-II semiconductor heterojunction with the off-set between the valence bands of the two materials being only slightly more than the binding energy of an exciton placed on either the TFB or F8BT polymer. As a result, an exciton on the F8BT side will dissociate to form a charge-separated (exciplex) state at the interface. [2, 3, 4, 16, 17]



Ordinarily, such type II systems are best suited for photovoltaic rather than LED applications. However, LEDs fabricated from phase-segregated 50:50 blends of TFB:F8BT give remarkably efficient electroluminescence efficiency due to *secondary* exciton formation in the back-reaction



as thermal equilibrium between the excitonic and charge-transfer states is established. This is evidenced by long-time emission, blue-shifted relative to the emission from the exciplex, accounting for nearly 90% of the integrated photo-emission.

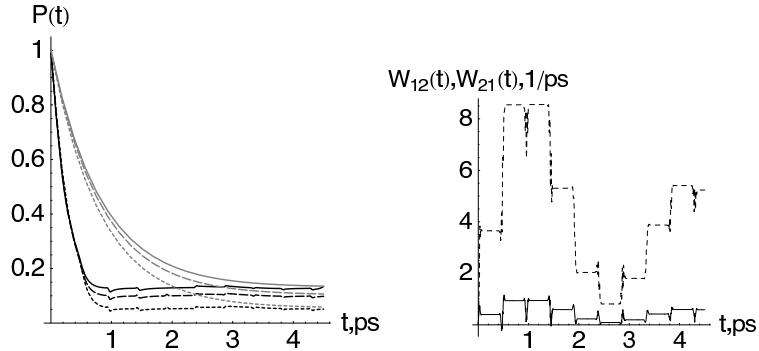


FIG. 2: (Left) The population of the excited state as a function of time for the TFB:F8BT heterojunction for three different temperatures obtained by solving the time-convolutionless master equation (black) or through the Marcus-type approximation (gray) at $T = 230\text{K}$, 298K , and 340K . (Right) Transition rates $W_{12}(t)$ and $W_{21}(t)$ for the TFB:F8BT heterojunction involving 24 normal modes at 298 K .

We consider only the two lowest electronic levels corresponding to

$$|XT\rangle = \text{F8BT}^* : \text{TFB} \quad \& \quad |CT\rangle = \text{F8BT}^- : \text{TFB}^+.$$

We take the vertical energies for these two states as $\epsilon_{CT} = 2.191\text{eV}$ and $\epsilon_{XT} = 2.294\text{ eV}$. As was shown in Ref. [18, 19, 20, 21], in poly-fluorene based systems, there are essentially two groups of phonon modes that are coupled strongly to the electronic degrees of freedom as evidenced by their presence as vibronic features in the vibronic emission spectra, namely: low frequency torsional modes with frequencies between 90 and 100 cm^{-1} and higher frequency C=C stretching modes with frequencies between 1500 and 1600 cm^{-1} [18]. The vibronic couplings within the model were determined by comparison between the Franck-Condon peaks of the predicted and observed spectra of the system.

As before, we consider the initial state as being prepared in the $|XT\rangle$ state corresponding to photoexcitation of the F8BT polymer. The results for the higher electronic level population obtained by numerically solving Eq. (23) are shown on Fig. 2. The time dependence of coefficients $W_{12}(t)$ and $W_{21}(t)$ is shown on Fig. 2. As in the previous example the electronic relaxation does not follow a simple exponential pattern. The main difference between this model and the previous example is that the electronic relaxation time is of the same order as the recurrence time for coefficients $W_{12}(t)$ and $W_{21}(t)$. As can be seen from Fig. 2 the time dependence of these coefficients has the form of approximately constant regions abruptly changed at regular recurrence intervals. This type of time dependence makes the electronic relaxation look like a series of exponential relaxations with changing rates. We do note, however, that transition rates $W_{12}(t)$ and $W_{21}(t)$ can become negative as the relaxation proceeds towards the

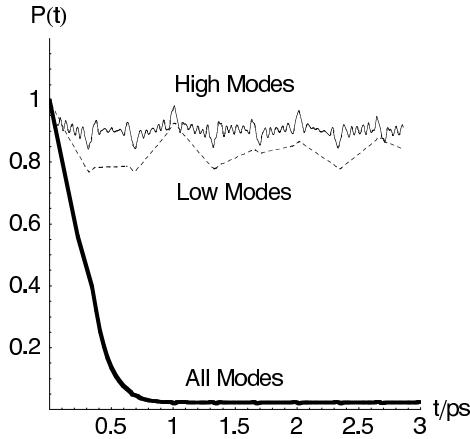


FIG. 3: Exciton population keeping only the high frequency (solid), low frequency, or using both high and low frequency phonon modes.

equilibrium population. As with any approximate method, this can lead to a lack of positivity in the populations.

Note also, that because the relaxation does not obey a simple exponential rate law, the initial decay slightly “overshoots” the final equilibrium population. This is most evident in the highest temperature case considered here ($T = 340\text{K}$). Since the $|XT\rangle$ is also the emissive state, photo-emission (not included herein) depletes this population on a nanosecond time scale (radiative lifetime). Population back-transfer from the $|CT\rangle$ to maintain a thermal equilibrium population then leads to the continuous replenishment of the emissive species such that nearly all of the CT population contributes to the formation of secondary (regenerated) excitonic states [4, 5, 14, 15, 16].

It is of interest to compare the relaxation dynamics in TFB:F8BT heterojunction obtained through the application of the time-convolutionless master equation with other approaches. As an example we will consider the Marcus-type approach which is widely used to study electron transfer in chemical systems [11, 14, 22, 23]. Based upon the model parameters, the driving force and reorganization energy are $\Delta E_{21} = 0.073 \text{ eV}$ and $E_\lambda = 0.092 \text{ eV}$, which places the system very close to the barrier-less regime as reported by Morteani, *et al* [3]. Because of the coordinate dependency of the coupling, some care must be taken in deriving the Marcus rates and we give details of this in the appendix. The results for the relaxation dynamics using these rates applied to TFB:F8BT heterojunction for three different temperatures are shown in Fig. 2.

It can be seen that apart from a more complicated time dependence the master equation approach gives faster relaxation when compared to the Marcus-type picture. The discrepancy between the two approaches can be explained by the

fact that the Marcus approximation is assumed to be valid when $kT \gg \hbar\omega_i$ for all the normal modes. In the case of the TFB:F8BT heterojunction this condition is not satisfied for the higher frequency modes.

Finally, we consider the contributions of each type of intramolecular motions to the charge-transfer process. Recall, our model included two non-overlapping bands of intramolecular phonon modes: a low frequency band corresponding to the torsional motions of the chain and a high frequency band corresponding to C=C bond stretching motions. In Fig. 3 we show the contribution of each band to the overall charge-transfer process. If we include only one band or the other, *very little charge transfer occurs* while if we include both bands, transfer occurs within the first 0.5ps following excitation. This emphasizes the fact that while one set of modes may be bringing the system into and out of regions of strong coupling between the XT and CT states (likely the high frequency modes), the other set of modes are required to help dissipate the energy associated with making the transition.

In conclusion, we present here a brief overview of a new approach we have developed for incorporating non-Markovian dynamics into the calculation of state-to-state transition probabilities for electronic systems. The time evolution of the electronic populations is, in general, more complex than the one obtained with the Pauli master equation and depends on the explicit form of the time dependent coefficients. The time-dependence of the rate coefficients introduces non-Markovian effects due to the vibrational motion into the electronic population transfers. What is currently lacking, however, is the inclusion of the electronic coherences and the important process of decoherence. Such contributions are quite important and we are currently extending our approach in that direction. While more complete and fully quantum approaches (such as MCTDH) permit highly detailed analysis of the dynamics of systems such as these, the computational cost associated with these approaches remains quite high.

Acknowledgments

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